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The Potential Applications of Nanoporous Materials for the Adsorption, Separation, and Catalytic Conversion of Carbon Dioxide

Gregor Sneddon, Alex Greenaway, and Humphrey H. P. Yiu*

Carbon capture and storage (CCS) technologies aiming at tackling CO₂ emission have attracted much attention from scientists of various backgrounds. Most CCS systems require an efficient adsorbent to remove CO₂ from sources such as fossil fuels (pre-combustion) or flue gas from power generation (post-combustion). Research on developing efficient adsorbents with a substantial capacity, good stability and recyclability has grown rapidly in the past decade. Because of their high surface area, highly porous structure, and high stability, various nanoporous materials have been viewed as good candidates for this challenging task. Here, recent developments in several classes of nanoporous materials, such as zeolites, metal organic frameworks (MOFs), mesoporous silicas, carbon nanotubes, and organic cage frameworks, for CCS are examined and potential future directions for CCS technology are discussed. The main criteria for a sustainable CO₂ adsorbent for industrial use are also rationalized. Moreover, catalytic transformations of CO₂ to other chemical species using nanoporous catalysts and their potential for large scale carbon capture and utilization (CCU) processes are also discussed. Application of CCU technologies avoids any potential hazard associated with CO₂ reservoirs and allows possible recovery of some running cost for CO₂ capture by manufacturing valuable chemicals.

hope for reducing these problems associated with greenhouse gases, but they may not be enough to avert the rise in CO₂ levels, which has recently reached a landmark of 400 ppm level.^[2] Therefore, development of CO₂ capture, storage and utilization (CCSU) techniques seems to be one obvious solution.^[1] However, one of the main problems associated with carbon capture and storage (CCS) is the fact that the process itself requires a certain amount of energy consumption, which leads to further emission of CO₂.^[3] Therefore, the aim of CCS is that through the development of more advanced CO₂ adsorption/absorption and adsorbent regeneration techniques this energy offset can be reduced, leading to a net reduction in CO₂ emission.

The energy sector accounts for the largest contributor to CO₂ emission (e.g., ≈40% of the total emission in the UK in 2011).^[4] Utilizing post-combustion CO₂ capture is important in order to lower the CO₂ emissions from large point sources of CO₂ such as power stations. To achieve this, an adsorption unit filled with a material (adsor-

bent) of high CO₂ absorption capacity can be integrated into the design of a new power plant or retrofitted into suitable existing power stations. The captured CO₂ will then be either transported to designated CO₂ reservoirs for storage or converted into other chemicals via carbon capture and utilization (CCU) technologies, which are still yet to be developed on an industrial scale.

Here, several families of nanoporous solids (including both “microporous” and “mesoporous” according to IUPAC’s definition) will be introduced. These materials all have a high surface area and pore volume for CO₂ adsorption, with a number of examples showing the selective adsorption towards CO₂ from a mixture of gases. The critical characteristics of the materials for an efficient CO₂ adsorbent will be described and the advantages and limitations of these materials to be used on an industrial scale will be discussed. The potential of CCU technologies associated with nanoporous materials as catalysts will also be highlighted.

1. Introduction

The emission of CO₂ from industry and power plants has become a worldwide problem with a strong link to global warming. It has been predicted by the International Panel for Climate Change (IPCC) that by the year 2100, the mean global temperature could rise by as much as 1.9 °C.^[1] Increasing our reliance on renewable energy sources and refining the energy production processes using fossil fuels have provided some

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2. Criteria for CO₂ Adsorbent Materials

At a low pressure, carbon dioxide behaves similar to many other gases (e.g., N₂ and Ar) in terms of adsorption onto a

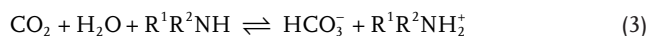
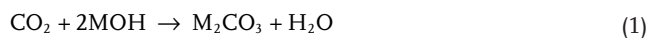
surface of a non-porous solid, following closely to the Langmuir model. Therefore, in theory, a solid-state adsorbent with a high surface area will have a high CO₂ adsorption capacity, but also a high adsorption capacity toward other gases (e.g., N₂) due to non-specific adsorption. As such, the adsorption efficiency of an adsorbent for CO₂ will be significantly reduced when the CO₂ content is low in a mixture of gases because of competitive adsorption against other major gaseous components. In a typical flue gas from a power station, CO₂ content is only ≈13% (coal-fired stations) to 8% (gas-fired stations).^[5] As a result, in order to achieve a high CO₂ adsorption efficiency, the adsorbent for post-combustion capture needs to have a high selectivity towards CO₂ over other gases present in the gas stream notably N₂ and H₂O. To design efficient adsorbents for CO₂, two common strategies are currently used, one targeting the physical property of CO₂ in terms of molecular dimensions and the other exploiting its chemical properties.

2.1. CO₂ Capture by Size Exclusion

To separate CO₂ from other gases in a mixture, a technology termed size exclusion can be used based on the difference in molecular dimensions of the components in the mixture.^[6] Size exclusion exploits the permeability theory but it is largely used to separate larger molecules in liquid phase, such as dialysis for the purification of biomolecules. The principle of separation for CO₂ relies strongly on the size, shape, connectivity and even the topography of the pores of an adsorbent material to create a stronger interaction towards one specific component in the mixture due to the close proximity of the surface to the target gas molecules.^[6] Zeolites, a family of microporous crystalline materials, have been widely used for this purpose due to their distinctive pore size/structure. Providing that they have distinctive pore dimensions, other microporous materials (e.g., carbon nanomaterials, metal organic frameworks) should also be capable for such separation.

2.2. Carbon Capture by Acid-Base Neutralization

Chemical properties of CO₂ can also be exploited for selective adsorption. Carbon dioxide can be considered as a weak acid and thus react readily with a base to form carbamates and carbonates, following the equations:



where MOH is an inorganic base (metal hydroxide) and R¹R²NH is an organic base, e.g., an amine.^[7] Since most other components (N₂, H₂O, unreacted O₂ and hydrocarbons) in the flue gas are neutral, use of an adsorbent of a basic nature can selectively adsorb acidic gas such as CO₂. However, there are two major issues to be considered for using a base as an adsorbent for CO₂. First, CO₂ is not the only acidic component in the

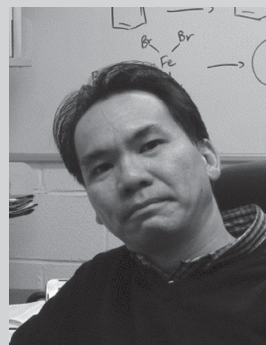


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flue gas. The other major acidic gas sources are SO₂ (if the flue has a high sulfur content) and NO_x. Increasing the concentration of these two acidic gases will reduce the efficiency of the CO₂ adsorption. Also, the adsorption force of CO₂ onto these

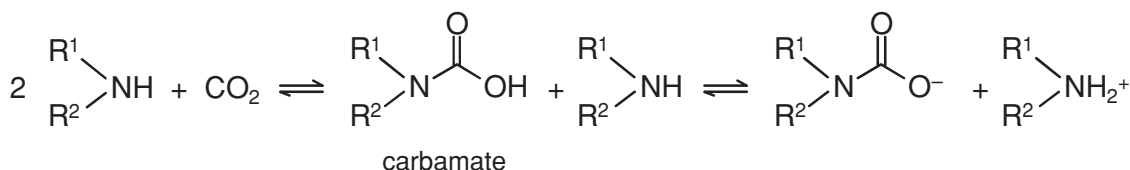


Figure 1. A two-step formation of carbamate from amines and CO₂.

basic adsorbent cannot be too strong so that the downstream removal of CO₂ and regeneration of active sites for adsorption is possible. For example, inorganic bases, such as calcium oxide CaO, have a high affinity towards CO₂, as well as other acidic species, but regeneration of these adsorbent is problematic (e.g., low regeneration efficiency) and energy intensive.^[8] Regeneration of CaO requires a high temperature of 900 °C and at this temperature, the surface area of the adsorbent is likely to reduce due to sintering, hence reducing the adsorption capacity and efficiency. Therefore, much research is currently directed towards the use of organic bases, which tend to be easier in regeneration at a low temperature but retain a high degree of affinity towards acid gases such as CO₂.^[9]

Aliphatic amines are among the most popular choice of organic bases as adsorbents for CO₂ adsorption via neutralization to form carbamates (see **Figure 1**). These can be free amine molecules,^[10] supported polyamine polymers,^[11] and grafted amine groups on a support material.^[12] Regardless of the form of amine, the principle of neutralization is essentially the same. For supported amine adsorbents, the adsorption efficiency highly depends on the basicity, the concentration of these basic sites and their accessibility, which can also be influenced by the structure of the support materials such as their porosity and pore connectivity.

2.3. Measuring the Capacity and Efficiency of a Sorbent for CO₂

To compare adsorption capacity and efficiency, standard methods with comparable parameters (reaction conditions including temperature and pressure) have been established. For solid adsorbents, it is common to measure the CO₂ adsorption capacity from a standard adsorption-desorption isotherm using pure CO₂. This can be carried out at 25 °C (298 K), 0 °C (273 K) or −78.5 °C (194.5 K) and a pressure of 1 atm (760 mmHg) or higher (≈5 atm). In general, the lower the adsorption temperature, the higher the adsorption capacity will be. However, some works report experiments carried out at a higher temperature (e.g., 75 °C) to mimic the flue gas condition or at higher

pressures. **Table 1** provides a comparison on the properties of various nanoporous adsorbent types considered to be suitable for CO₂ adsorption.

For basic adsorbents using neutralization, the maximum CO₂ adsorption capacity can also be estimated stoichiometrically, assuming 100% efficiency. For instance, the CO₂ adsorption capacity of calcium oxide CaO can be estimated to be ≈17.86 mmol g^{−1} using the following equations:



$$\text{CO}_2 \text{ adsorption capacity (in mmol g}^{-1}\text{)} = \frac{\text{sorbent/CO}_2 \text{ stoichiometric ratio}}{\text{formular weight of sorbent}} \times 1000 \quad (5)$$

Using this method, we can estimate the maximum capacity of all bases, liquids or solids. Therefore, ammonium hydroxide solution (≈30% w/w) will have a maximum CO₂ adsorption capacity of 8.8 mmol g^{−1}, while that of BeO solid can be as high as 37.0 mmol g^{−1}, which is probably the material available with the highest theoretical CO₂ adsorption capacity via neutralization. Unfortunately, this estimation assumes a 100% stoichiometric reaction and it is unlikely to happen, particularly for solid, non-porous adsorbents such as CaO, due to the accessibility of sites. Therefore, the experimental data are usually much lower than these values. For amine adsorbents, normally it is assumed that two amine groups will react with one CO₂ molecule to form the more stable carbonate species (see **Figure 1**). Therefore, the N/CO₂ ratio provides a certain degree of indication on how efficient an amine-based adsorbent is. On the other hand, the efficiency of CO₂ adsorption for an adsorbent can be derived from the experimental and theoretical maximum adsorption capacity as follows:

$$\text{adsorption efficiency (\%)} = \frac{\text{experimental capacity}}{\text{theoretical maximum capacity}} \times 100\% \quad (6)$$

Table 1. Comparison on the CO₂ adsorption properties among nanoporous materials.

Nanoporous material	Typical range of capacity [mmol g ^{−1}] at 1 bar, 25 °C	Adsorption mechanism	Quantity produced per batch	Ref.
Zeolites	1.5–4.0	Interaction with metal ions (e.g., K ⁺ , Na ⁺)	Tones	[13]
MOFs	1.0–7.0	Physisorption and chemisorption	100–500 mg	[14]
Mesoporous silica	1.0–2.0	chemisorptions onto basic groups (e.g., amines)	1–5 g	[13]
Carbons (CNT, mesoporous carbon)	0.5–3.0	Physisorption (except amine-functionalized CNT)	<1 g	[13]
Organic cage framework (OCFs)	1.0–5.0	Physisorption and chemisorption	<1 g	[15]

This value indicates how many basic sites, such as the number of amine groups on an adsorbent, are engaging with CO₂ molecules.

2.4. Other Considerations

In addition to the adsorption characteristic, there are several factors regarding practicality for a material to be a suitable adsorbent for CCS applications. For examples, i) the adsorbent material needs to be easily regenerated, and reusable, ii) the material should be stable (physically and chemically) under the operational conditions (this includes thermal stability and moisture sensitivity), iii) the material needs to be readily available and economically viable (e.g., BeO shows a high theoretical adsorption capacity but beryllium is a rare element, so large-scale applications become unlikely), iv) the manufacture of adsorbent can be scaled up, and v) the material has to be of low toxicity, easy to handle and harmless to the environment upon disposal. All these factors are also influenced by the size of the operation, type and design of the power station, and other environmental factors.

3. Current CO₂ Capture Technology in Industries

In the industrial sector, the most widely applied CO₂ separation technology would be chemical absorption (instead of adsorption on solids) with an aqueous solution of alkanolamines such as monoethanolamine (MEA) and diethanolamine (DEA). These amine solvents reacts readily with acidic gases including CO₂, making them popular CO₂ absorbents.^[10] However, complications associated with the use of liquid amines such as corrosion on equipments, oxidative degradation of absorbents, flow problems caused by increasing viscosity with fast-reacting amines and relatively high energy consumption^[16] suggest that this method is far from ideal. In addition, since most CO₂ absorption

systems are designed as stripping columns, the overall efficiency of the conventional stripping tower is subject to mass-transfer limitations (see Figure S1, Supporting Information).

Among these amine solvent systems, the most extensively used in CO₂ absorption is the MEA absorption process, e.g., post-combustion removal of CO₂ from the flue gas stream in the natural gas industry. In this absorption process, the MEA solution is required to be in contact with the flue gas in an absorber column, reacting with CO₂ to form MEA carbamate in solution. The CO₂-rich MEA solution is then sent to a stripper where the solution is reheated to release pure CO₂.^[17] However, this is an expensive process as it requires an intensive energy input for absorbent regeneration and large process units. In the literature, it is estimated that the heating cost during solvent regeneration constituted up to 70% of the total operating costs in a CO₂ capture plant.^[18] Considering all these problems associated with amine solvent absorptions, the next generation of CO₂ capture systems are rapidly required for advancing CCS technologies.

4. Nanoporous Materials for CO₂ Capture

One possible solution to overcome the limitations of current liquid amine processes is using solid adsorbents. Generally, solids are easier to handle and impose fewer problems associated with corrosion. In order to maximize the adsorption capacity, these solids need to possess a high specific surface area (surface area per mass of material, in m² g⁻¹). Because of this, nanoporous materials will be among the most suitable solid adsorbents for CO₂. These materials usually have a high specific Brunauer–Emmett–Teller (BET) surface area (500–2000 m²g⁻¹) and a high pore volume (0.5–1 cm³g⁻¹), leading to a high theoretical adsorption capacity. **Figure 2** shows an illustrative comparison on the pore size for selected nanoporous materials. Also, many of these materials (e.g., carbon and silica based materials) are thermally stable up to

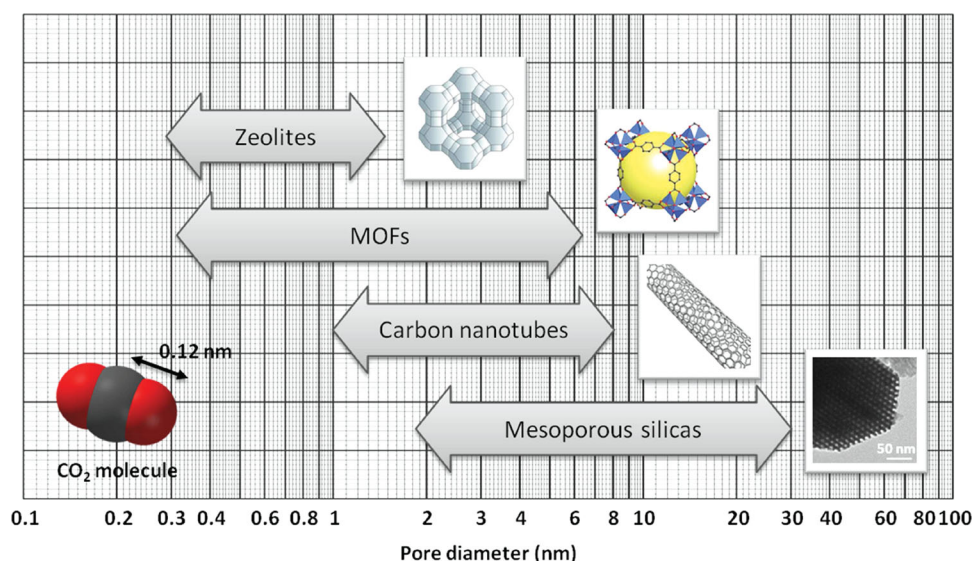


Figure 2. Illustrative comparison on the pore sizes of several common nanoporous materials.

150–200 °C, an essential property for post-combustion capture as the discharged flue gas from a power plant can be at an elevated temperature (40–120 °C).

4.1. Zeolites

Zeolites are aluminosilicate minerals with ordered, nanoporous structures. They can be found naturally, prepared industrially or synthesized in laboratories. Because of their high surface area (e.g., 571 m²g⁻¹ for zeolite 13X), specific porous structures and availability in large quantities, zeolites have been widely used in industry as adsorbents and catalysts. The pore size of zeolites is usually ranging from 3–12 Å (0.3–1.2 nm). Inside the smaller pores, guest molecules (adsorbates) of a comparable size can strongly interact with the walls of the pores. Structures of selected zeolites (X, Y, A, and rho) are shown in Figure 3a.

Considering the size of a CO₂ molecule (≈5.4 Å in length and 3.1 Å in diameter), zeolites with a pore size of 4–5 Å can be highly affinitive to CO₂. However, similar attractive forces can also be seen towards other gaseous adsorbates such as N₂ and H₂O. Therefore, the basicity of zeolites becomes the key property for selective adsorption of CO₂ over N₂ and H₂O.

The basicity of a zeolite can be created by ion exchanging with cations of alkali metals (Group 1A). Usually, the basic strength increases following the order: Cs⁺ > Rb⁺ > K⁺ > Na⁺ > Li⁺.^[19] However, this trend does not always reflect the CO₂ adsorption capacity of a cation exchanged zeolite. For example, a study on cation exchanged ZSM-5 zeolites showed the CO₂ adsorption capacity with the order of Li⁺ > Cs⁺ = Rb⁺ > K⁺ = Na⁺ at 303 K (30 °C) and Rb⁺ > K⁺ > Na⁺ > Li⁺ > Cs⁺ at 333 K (60 °C), both measured at 200 kPa (≈2 atm).^[20] This is because the size of cation affects their distribution in the pores of zeolites while their polarity also affects the polarization of adsorbed

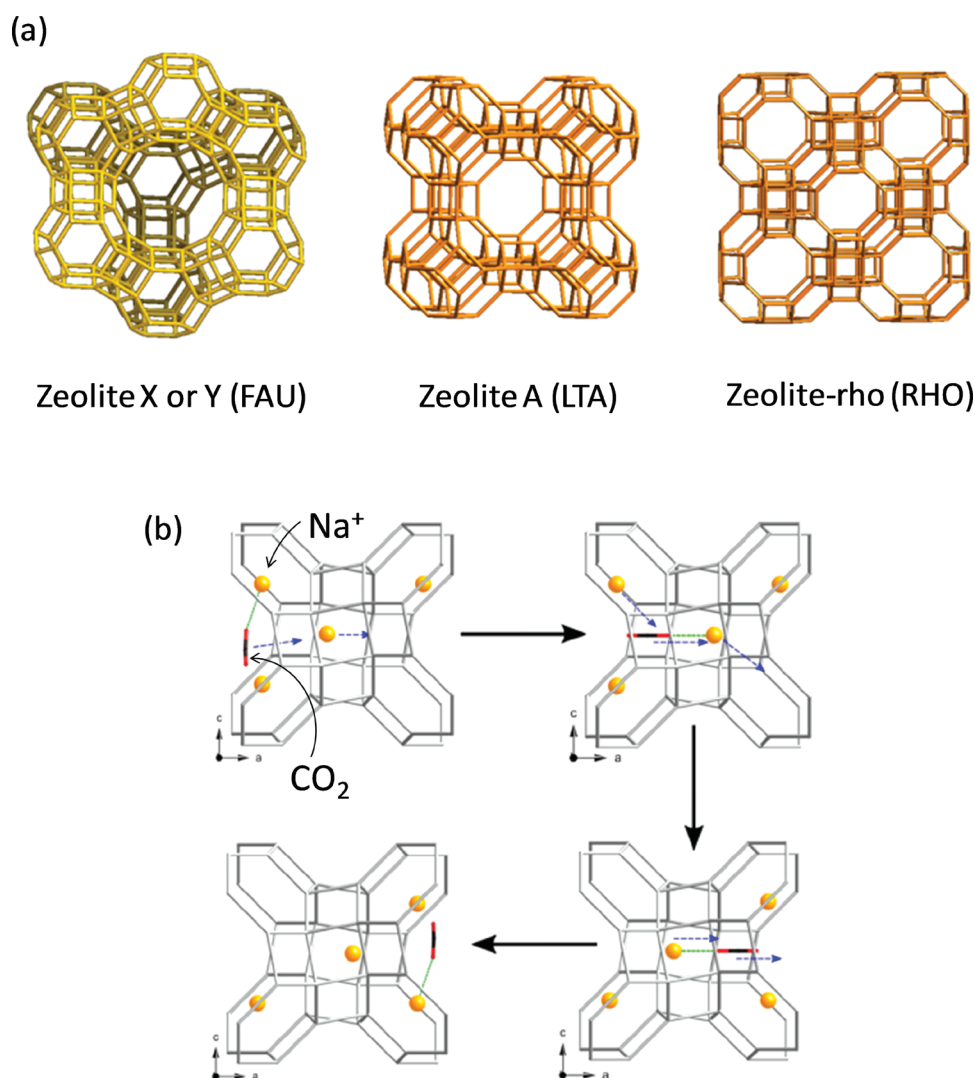


Figure 3. a) Structures for zeolite X and Y (both have the same faujasite FAU structure), zeolite A, and zeolite-rho (structures from IZA Structure Commission, www.iza-structure.org). b) Postulated cooperative mechanism by which CO₂ molecules (represented by red and black sticks) could pass through a window site between a-cages in zeolite Na-rho, where a Na⁺ cation (yellow sphere) occupies one of the S8R sites in the window. Reproduced with permission.^[25] Copyright 2012, American Chemical Society.

CO₂.^[21] Another factor influencing the CO₂ adsorption capacity of a zeolite is the Si/Al ratio, which is also related to the total cation exchange capacity, leading to the total amount of cations in the structure. A lower Si/Al ratio (see note in the Supporting Information) gives a higher cation exchange capacity and therefore more cations will be available for interacting with the CO₂ molecules, hence a higher adsorption capacity. Moreover, the pore size of zeolites also has an effect on the CO₂ adsorption capacity, as well as the rate of adsorption. At a low pressure, such as ambient pressure, smaller pores tend to show a higher affinity to CO₂ over N₂ and O₂, based on a study using zeolites A, X and Y as the adsorbents.^[22]

Recently it has been discovered that some small pore zeolites show an enhanced ability to selectively adsorb CO₂ over N₂ or CH₄ due to a “molecular trapdoor” mechanism.^[23] Zeolites exhibiting this molecular trapdoor mechanism contain super cages that are accessible through eight-membered rings (8MR)^[24] or double eight-membered rings (d8MR).^[25] The windows formed by the 8MR or d8MR are large enough to allow small molecules, such as N₂, O₂, CO₂ and CH₄, to pass through, but these windows become effectively blocked by cations which adopt the energetically most favorable position at the center or face of the window. For a molecule to pass through the window the cation has to first move away from its position and this is achieved by a favorable interaction between the cation and certain guest species.

This temporary and reversible trapdoor mechanism starts as a closed gate becoming opened when the “gate keeping” cation interacts favorably with a guest species causing a reduction in the energy barrier and moving away from the center of the window. When the cation is situated at the “open” position, guest species molecules are capable to pass through the window and move into the next cavity within the zeolite structure. As the guest molecules diffuse into the adjacent cages inside the zeolite, the force holding the cation at the open position decreases and the cation moves back to its original position, closing the gate (see Figure 3b). This trap door mechanism will only occur with guest species that can interact strongly and favorably with the gate keeping cations, such as CO₂ with K⁺, and it will not occur with weakly interacting species such as N₂ and CH₄ as the energy barrier is too high to cause the cation to move away from the gate keeping site. Since such selectivity depends on the interaction between the gate keeping cation and guest species (CO₂ in this case) rather than the size of the guest species, molecular trap door zeolites allow for the possibility of inverse size discrimination so should be viewed as an independent selection mechanism that is separated from the molecular sieving (or size exclusion) mechanism. The high levels of selectivity exhibited by the molecular trapdoor zeolites reported so far suggest that other zeolites that contain 8MR or d8MR such as zeolite A (LTA)^[26] and ZK-5^[27] may also exhibit similar adsorption properties.

The conventional method to analyze the performance of a zeolite sample, as well as most newly developed adsorbent materials, as a potential CCS material is to acquire gas isotherms at a set of relevant temperatures and pressures for the gases present in the mixture from which CO₂ is to be removed. However, as has been suggested, relevant temperatures and pressures for different systems can vary widely. For example,

conditions for post-combustion capture, where the major separation is between CO₂ and N₂, are significantly different from that for pre-combustion capture, where CO₂ is to be separated out from H₂ or CH₄. Indeed even among post-combustion capture systems at different power stations there can be subtle differences, such as the CO₂ concentration in flue gas from a gas-fired station to that from a coal-fired station as discussed earlier. These issues coupled with the advanced synthesis methods to rapidly generate a variety of cation exchanged species (e.g., K⁺ and Na⁺) of many different zeolites mean that a large quantity of gas adsorption isotherm data need to be collected for a comprehensive analysis on one single type of materials.^[25] Therefore a significant bottle-neck for CO₂ adsorption studies using new zeolite-based adsorbent materials is the availability of access to efficient gas adsorption instrumentation. As a result instrument manufacturers are attempting to develop automated high throughput gas adsorption analyzing units. One notable example of which is a volumetric technique that can analyze 28 samples in parallel recently developed by Wildcat Discovery Technology Inc.^[28] This apparatus has recently been demonstrated in a high throughput study of cation exchanged forms of zeolites Na-A (LTA) and Na-X (FAU) for use in CCS, with the results acquired from the high throughput analyzer validated against data acquired from a conventional Micromeritics ASAP 2020 gas adsorption analyzer.^[29]

Zeolites have already been widely used in many industrial processes. However, their application in CO₂ capture from power plant flue gas has not been as successful. This is likely because zeolites can be deactivated by moisture, leading to a significant reduction in CO₂ adsorption capacity. One possible explanation for this phenomenon is that water can reduce the strength of the local electric field on the cation sites.^[30] Since water is an inevitable product from combustion, cation exchanged zeolites are considered to be ineffective unless the moisture content is removed prior to CO₂ adsorption, or prevented from entering the zeolite by some other means. There are, for example, several reported attempts at forming a waterproof coating for zeolites, which have had a highly hydrophobic surface layer chemically bound to the zeolite crystallites in a post-synthetic process.^[31]

4.2. Metal-Organic Frameworks (MOFs)

Metal-organic frameworks (MOFs) are ordered structures constructed with both inorganic and organic species. In general, MOFs are comprised of transition metal ions, free or in clusters, interconnected with organic struts, or ligands.^[32] These organic ligands are usually molecules with aromatic groups (providing rigidity) terminated with functional groups capable of coordinating to these metal ions (coordination bonds). The functional groups can be carboxylic acid groups^[33] or heterocyclic aromatic rings incorporated with nitrogen atoms (e.g., pyridine),^[34] but other coordinating functional groups such as phosphonates have also been used to form MOFs.^[35] Many MOF systems show nanoscale porosity, resulting in a large internal surface area, with a variety of window sizes.^[32] Similar to zeolites, these properties can lead to a wide range of applications, including: drug delivery, chemical sensing, ion exchange,

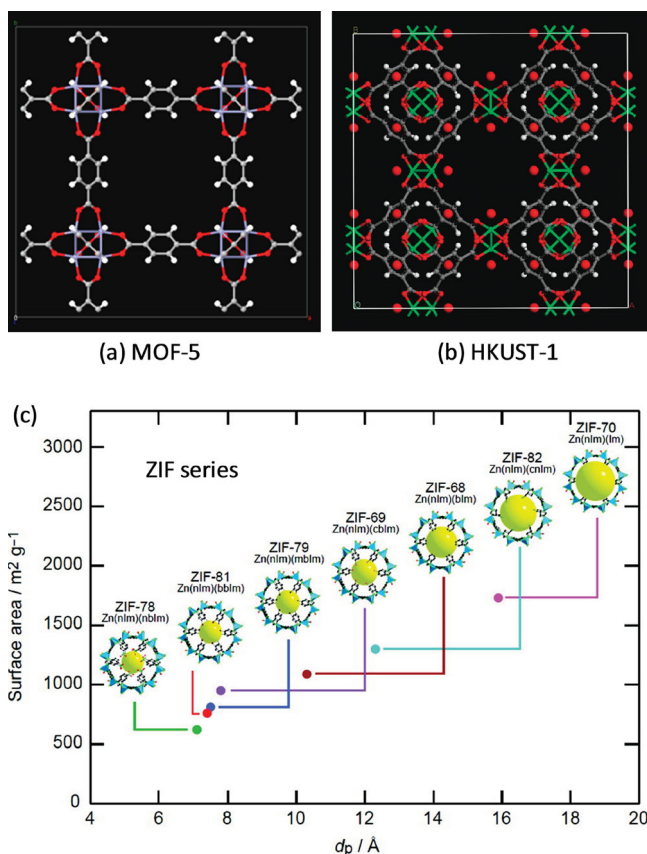


Figure 4. The structure for a) MOF-5 (structure from MOFomics structure simulation website) and b) HKUST-1. Reproduced with permission.^[55] Copyright 2009, American Chemical Society. c) Plot of pore diameter (d_p) vs. surface area for the ZIF series, indicating a nearly linear relationship. Among them, ZIF-78 showed the highest selectivity for CO_2 over N_2 ($S = 396$) (see Table 2). To illustrate the variation of the poresize and functionality, the *kno* cage of each ZIF is shown in yellow. Reproduced with permission.^[53] Copyright 2009, American Chemical Society.

chemical catalysis, molecular separations and gas storage.^[32] One of the major advantages of MOFs over other solid porous adsorbent materials is the possibility to tune systems to carry out a particular task by varying the size and nature of the components used in the synthesis. For example, the pore size of a MOF system can be controlled by changing the length of the struts. The ability to generate a whole series of MOFs sharing the same type of connectivity is known as “isorecticular” synthesis and notable examples include the MOF-5 (structure shown in Figure 4a)^[36] and NOTT-11 series.^[37] Such unique structural tunability of MOFs enables them to be considered as promising candidate materials as adsorbents for CCS applications, and therefore, many studies in this area can be found in the literature.^[38–41]

For instance, MOFs have been studied for selective CO_2 adsorption over N_2 . As pointed out previously, in post-combustion CO_2 capture the primary gas separation occurs between CO_2 and N_2 at a slightly elevated temperature of around 40 °C (313 K) and at ambient pressure. The composition of the flue gas varies depending on the hydrocarbon source, but a typical composition is 15% CO_2 , 75% N_2 , 7% H_2O with the remainder

being made up with contaminants such as SO_x , NO_x , O_2 and CO . For the purpose of post-combustion CO_2 capture, an idealized material would exhibit a high selectivity to CO_2 over N_2 as well as a good volumetric and gravimetric uptake of CO_2 . With these requirements, several MOFs performed well, with the isomorphous CPO-27 series showing very high levels of uptake with a good selectivity^[42] while HKUST-1 (structure shown in Figure 5b) giving one of the best selectivities,^[43] calculated by dividing mass of CO_2 at 0.15 bar by mass of N_2 at 0.75 bar.^[44]

One method that has been investigated in detail as a route to improve CO_2 against N_2 selectivity is to generate MOFs with functionalized pores, as the addition of polarizing groups enhances interactions with the CO_2 molecules. For example, a study on using cobalt adeninate bio-MOFs for selective adsorption of CO_2 was reported by An et al.^[39] With the multiple nitrogen Lewis base groups, adenine showed a high capacity for CO_2 uptake. The basic nature of the coordinating ligand allowed a CO_2/N_2 selectivity of 81:1 at 0 °C and 75:1 at 25 °C, with a total CO_2 adsorption capacity of 6 mmol g^{-1} and 4.1 mmol g^{-1} at 0 °C and 25 °C respectively.^[39] Other example of MOFs, triazolate-bridged systems functionalized with ethylenediamine, were also studied for selective CO_2 adsorption at low pressure.^[40] These MOF systems showed excellent stability in moist and acidic conditions, an advantage over most zeolite adsorbents. Combined with the improved low-pressure performance over the standard triazolate-bridged MOFs, they are ideal for dealing with real flue gas environments. At pressures of up to 0.06 bar (6 kPa, ≈ 0.06 atm) CO_2 the ethylenediamine modified MOFs showed an enhanced capacity of 0.366 mmol g^{-1} from 0.277 mmol g^{-1} for the standard sample, an improvement of over 30%.^[40]

MOFs with small pores showing selectivity based upon a molecular sieving principle are less common as the pore dimension needs to be finely tuned to allow CO_2 but not N_2 or CH_4 to diffuse into the framework. However, a recent investigation into the functionalized forms of Sc_2BDC_3 (scandium terephthalate) yielded interesting results for the $-\text{NO}_2$ (nitro) functionalized framework.^[45] Interestingly, the single crystal structure of $-\text{NO}_2$ functionalized Sc_2BDC_3 suggested that it does not appear to contain any pores large enough to allow CO_2 or N_2 to adsorb. Nonetheless, it does show appreciable CO_2 uptake (≈ 1.0 mmol g^{-1} at 25 °C) while it adsorbs a negligible amount of N_2 , making it an extremely selective MOF system for CO_2 against N_2 . The possible explanation for such selectivity exhibited is a size exclusion process in which the $-\text{NO}_2$ groups effectively block the pores to the bulbous N_2 molecules while the longer more polarizing CO_2 molecules are able to manipulate the $-\text{NO}_2$ groups enough to move through the pores and become adsorbed inside the MOF structure.

For pre-combustion CO_2 separation, the primary gas separation required is different from that in post-combustion CCS, and therefore the requirements/properties of the adsorbents also changes. For example, in pre-combustion, the major separation is between CO_2 and H_2 and arises after a hydrocarbon source having undergone a syngas shift followed by a wet syngas transformation. The conditions for measuring the optimal adsorbent performance should be at approximately 40 °C and between 5 and 40 bar pressure. It is likely that a pressure swing adsorption mechanism for the removal of adsorbed

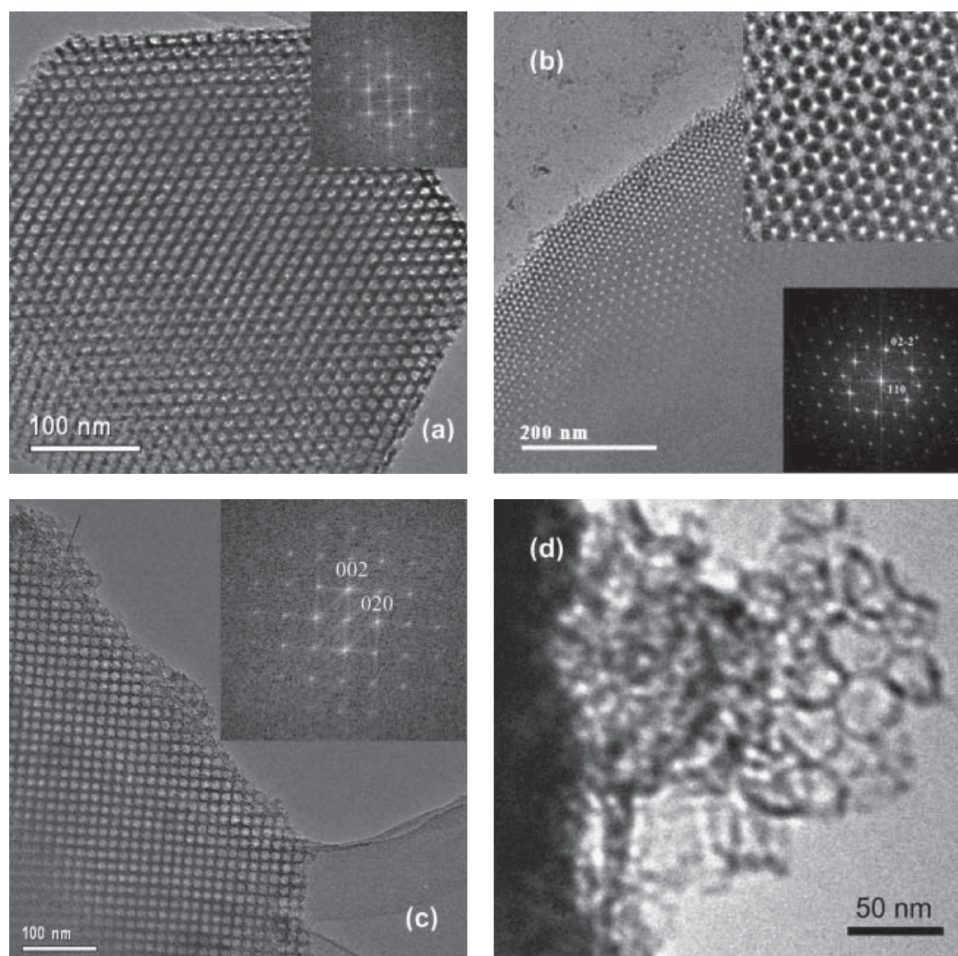


Figure 5. TEM images showing structures of a) SBA-15 ($p6mm$), b) FDU-5 ($la3\sim d$), c) FDU-12 ($Fm3m$) and d) MCF. Reproduced with permission.^[64] Copyright 2005, Royal Society of Chemistry.

CO₂ would be most applicable to a pre-combustion CCS system. Therefore a material showing a low initial uptake can be beneficial as it would not require the system to undergo a significant pressure drop to release the stored CO₂.^[46]

As we can appreciate, the ability for selective CO₂ adsorption in a gaseous mixture determine whether a MOF system is a suitable candidate for use in CCS, as well as having a scalable synthesis and ability to adsorb/desorb CO₂ in a rapid timescale. However, experimentally it has been difficult to directly measure adsorption selectivity, between CO₂ and N₂ for example, and methods to study adsorption-desorption cycles on small samples have been lacking. Recently, there has been some progress made in both of these areas, enabling more thorough investigation of MOFs for use in CCS. Similar to assessing zeolites, CO₂ gas adsorption at a chosen temperature is commonly used for studying the CO₂ adsorption property for MOFs. Such studies can be carried out either gravimetrically (in which the mass of the sample is measured as it increases due to adsorbed gas) or volumetrically (in which the sample is exposed to a certain dose of the adsorbate gas and the difference between the equilibration pressure is measured, yielding the amount of the gas adsorbed). Unfortunately, gas adsorption isotherms can only be measured using single gas components

as it is impossible to deconvolute results obtained when a multi-component system is used. As mentioned previously, adsorption selectivity for simulated post combustion systems is often estimated indirectly by dividing the uptake of CO₂ at 0.15 bar by the uptake of N₂ at 0.75 bar.^[44] This method could lead to uncertainty and inaccuracy as the adsorption behavior of an adsorbent can be different at a multi-component gaseous environment.

Recently scientists working on MOFs have reported a breakthrough (the course for a gas to go past a bed of adsorbent) experiment for studying the separation of CO₂ from mixtures in N₂ or CH₄.^[47,48] During this new experiment a column was packed with pelletized sample, which was then purged with an inert gas (e.g., He) to remove any water or other adsorbed species. The sample was then exposed to a stream of gaseous mixture, such as 15% CO₂ with 85% N₂. The composition of the gas flow exiting the column was then monitored by mass spectrometry. As such, it was possible to calculate retention times of the gas components exposed to the sample and therefore their relative adsorption properties (see Figure S2, Supporting Information). By conducting a series of these breakthrough experiments, van Baten et al. compared the CO₂ capture characteristics of several MOFs and zeolites.^[47] Among the MOFs tested,

Table 2. Selectivity (sorbent selection parameters, S) of selected examples of zeolites and MOF systems for CO₂ against nitrogen or methane.

Absorbent	Pore size [nm]	BET surface area [m ² g ⁻¹]	CO ₂ adsorption capacity ^{a)} [mmol g ⁻¹]	Sorbent selection parameter (S) ^{b)}		Ref.
				CO ₂ :N ₂ = 1:9	CO ₂ :CH ₄ = 1:1	
Zeolite-5A	0.5	506	3.5	163	–	[50]
Zeolite-13X	0.11	616	2.49 (3.97)	128	19.1	[51]
ZIF-78	0.38	620	0.58	396	–	[52]
ZIF-79	0.4	810	0.26	83	–	[52]
ZIF-81	0.39	760	0.27	101	–	[52]
ZIF-82	0.81	1300	0.41 (1.42)	105	20.5	[52]
Mg-MOF-74	1.11	1542	(7.23)	–	23.5	[53]
Ni-MOF-74	1.11	1218	4.34 (6.23)	83.5	21.0	[53]
HKUST-1	0.35	1571	(0.62)	–	19.8	[54,55]

^{a)}CO₂ adsorption capacity measured at 1 atm (CO₂:N₂ = 1:9) and 25 °C, values in brackets indicate CO₂:CH₄ = 1:1 conditions; ^{b)}Using a vacuum swing adsorption process. Adsorption pressure = 1 bar, desorption pressure = 0.1 bar.

only Mg-MOF-74 consistently outperformed the majority of the zeolites selected for the study.

One of the major advantages for using these breakthrough experiments over commercial volumetric or gravimetric adsorption techniques is the much shorter time required to run a dynamic separation from a mixed gas composition. Depending on the sample and experiment protocol, a breakthrough separation can occur on a few minutes timescale (as opposed to approximately a day to complete an adsorption-desorption isotherm), which allows for repeated experiments to be conducted after a regeneration period, usually at elevated temperatures under inert gas flow (e.g., 150 °C under flowing He). This also allows two further critical performance criteria to be investigated. First, regeneration capacities of the sample can be studied as a function of temperature or number of cycles. Furthermore the level of humidity present in the gas streams can be regulated enabling studies on any potential loss of adsorption performance due to water. For example, Remy et al. have reported that the performance of Mg-MOF-74 decreased upon the cycling of humid CO₂ in a linear manner as the number of cycles increased, a result that could have important ramifications for the suitability of Mg-MOF-74 as a potential CCS adsorbent.^[48]

Another selectivity study has also been carried out by collating data from many reports on using MOF systems for CO₂ specific adsorption.^[41] During separation of CO₂ from the flue gas stream using a vacuum-swing adsorption (VSA) regeneration process, MOFs were also found to be less efficient than zeolites. At specific conditions such as a 10:90 mixture of CO₂:N₂ with an adsorption pressure of 1 bar (≈1 atm) and desorption pressure of 0.1 bar (≈0.1 atm), generally, MOFs were found to have a lower CO₂ adsorption capacity than zeolites but a greater potential for regeneration. One parameter used for evaluation of the MOFs was the sorbent selection parameter (S),^[49] which is a combination of the adsorption selectivity and working capacity, and is defined as

$$S = \frac{\Delta q_1}{\Delta q_2} \left(\frac{q_{m1} b_1}{q_{m2} b_2} \right) \quad (7)$$

where q_i is the amount adsorbed (in mmol g⁻¹); q_{mi} is the monolayer saturation amount (in mmol g⁻¹); and b_i Langmuir parameter (atm⁻¹).

The S values of selected zeolites and MOF materials are summarized in **Table 2**. Based on these S values, the most promising MOF materials for CO₂ adsorption using these criteria were found to be the zeolitic imidazolate frameworks (ZIF's) as well as Ni-MOF-74. Although the CO₂ adsorption capacities for these materials were relatively low in comparison to the zeolites, their S values were similar. In particular ZIF-78 showed a large S value indicating its suitability towards flue gas treatment. Figure 5c shows the relationship between the surface area and the pore diameter of the ZIF series. Results from Table 2 also suggested that both zeolite samples outperformed MOFs in terms of selectivity towards CO₂, except ZIF-78. Recently, a series of MOF systems built with SiF₆²⁻ anions (SIFSIX) showed an outstanding selectivity towards CO₂ (up to 1700 at 1 bar) over N₂, over four times higher than that of zeolite 13X.^[56] Moreover, their selectivities for CO₂ over CH₄ and H₂ (350 and 1800 respectively) were also remarkable, making these SIFSIX materials suitable for both pre- and post-combustion CO₂ capture. Therefore, SIFSIX MOFs can be considered as a showcase adsorbent for carbon capture.

One of the disadvantages of using breakthrough experiments for selectivity measurements is the requirement for a relatively large quantity of sample (around 5 g), which can be troublesome to achieve for certain MOFs. Therefore to test the regeneration capabilities of MOFs on a much smaller sample size a new technique based on thermogravimetric analysis (TGA) has been successfully reported.^[50] In this work, a sample of 10% Ni(OAc)₂/H₃PO₃-modified Mg-MOF-74 was repeatedly cycled (10 times) in alternating flowing argon at 493 K (220 °C) and CO₂ at 313 K (40 °C) in a TGA instrument, during this time the mass gain and loss for the sample was measured and used to calculate a working uptake capacity for CO₂ of 6.1 mmol g⁻¹.

In many reports, MOFs have been regarded as some of the best candidates for the ultimate task of CO₂ capture due to their high adsorption capacity, selectivity and recyclability. However, at the moment, use of MOFs for large scale processes, such

as industrial catalysis and CCS, is still far from feasible. One major limitation to using MOFs is that only small quantities, usually <1 g per batch, of the active material can be synthesized although production of a MOF material at an industrial scale has been reported.^[57] Moreover, probably the least considered factor, the environmental impacts of MOFs cannot be ignored, particularly if they are to be used on an industrial scale. Many MOF systems are built using toxic transition metals (Co, Ni, Mn, Cu) and ligands (aromatic and/or heterocyclic compounds) and these materials may cause serious environmental issues upon disposal. Unfortunately, research on the environmental impacts of MOFs has been widely overlooked.

4.3. Functionalized Mesoporous Silicas

In the early 1990s, the discovery of ordered mesoporous silica materials (MCM-series, SBA-series and MCFs, structures shown in Figure 5)^[58] opened up many new research directions in separation,^[59] catalysis,^[60] even biotechnology.^[61] Because of their high surface area ($\approx 1000 \text{ m}^2 \text{ g}^{-1}$) and high pore volume ($\approx 1 \text{ cm}^3 \text{ g}^{-1}$), these mesoporous silicas have been used as a sorbent for many species including gases,^[62] organic pollutants^[63] and biomolecules.^[64] Unlike zeolites and MOFs, the larger pore size (>2 nm or >20 Å in diameter) of mesoporous silicas implies that, without modification, the intrinsic interaction between the guest molecules and the adsorbent is weaker, particularly at low pressure. Moreover, selective chemisorptions of CO_2 is also difficult as the surface of mesoporous silica is covered with mildly acidic silanol groups ($-\text{Si}-\text{OH}$). Therefore, surface modification is required if mesoporous silicas are to be used for CO_2 capture. Generally, two possible modification routes are used for this purpose; impregnation of basic nano-sized crystals (alkaline or alkaline earth metal oxides) and grafting organic groups with basic characters such as amines.

Mesoporous silicas have been used to support transition metal oxide particles (e.g. iron oxides,^[65] titania TiO_2 ,^[66] and zirconia ZrO_2 ^[67] for catalytic purposes, and alkaline earth metal oxide particles (CaO ^[68] and MgO ^[69]) to provide a basic surface for CO_2 chemisorption. Although a good CO_2 capacity has been shown from these composite materials (up to 10 mmol g^{-1}), the sustainability of these composite materials is questionable. Firstly, they were synthesized from calcium and magnesium salts, which are likely to be manufactured from carbonates (CaCO_3 or MgCO_3 , both are common natural minerals) with a substantial CO_2 emission, at a stoichiometric ratio of 1, in addition to the energy required to decompose the carbonates or to manufacture the strong acids (e.g., HNO_3) required for the preparation of these basic adsorbents. Secondly, regenerating materials requires a high temperature (700–900 °C) due to the high thermal stability of CaCO_3 and MgCO_3 . Unless the source of CO_2 for capture has a high temperature and requires a thermally stable adsorbent, these materials are unlikely to be practical for most CCS applications.

Since the associated energy consumption of using purely inorganic mesoporous silicas, modified with CaO or MgO , for CCS is too high to be realistic, organic-inorganic hybrid mesoporous silicas were developed for this purpose. As early as mid-1990s, silanization methods have been introduced for the

synthesis of organic-inorganic hybrid mesoporous silica, using functionalized alkoxysilanes.^[70] One of the most commonly used alkoxysilanes, 3-aminopropyltriethoxysilane or APTES, has been used for grafting amine groups onto the mesoporous silica surface.^[71] These basic amine groups can also provide strong affinity towards CO_2 and other acidic gases. Depending on the conditions of measurement and the preparation method, the CO_2 adsorption capacity of amine-functionalized mesoporous silica ($\text{NH}_2\text{-MCM-41}$, $\text{NH}_2\text{-SBA-15}$ or $\text{NH}_2\text{-MCF}$) varies from 0.5 to 2.0 mmol g^{-1} at 25 °C and 1 atm. Results from selected publications using amine functionalized mesoporous silica for CO_2 adsorption are summarized in Table 3. In general, the CO_2 adsorption capacity increases when the water content (either on the adsorbent surface or the gas) increases due to the formation of the protonated ammonium ions and carbonates.^[87] This observation is opposite to that from cation exchanged zeolites, which can be easily deactivated by water. For post-combustion CO_2 capture from flue gas where high moisture content is likely, this could be a distinctive advantage. Furthermore, such resistance to deactivation due to water has the added benefit that supported amines on mesoporous silicas could be used in a temperature swing adsorption (TSA) CCS system based on a steam heating regeneration cycle. This is unlikely to be applicable to either MOFs or zeolites since both can rapidly degrade in the presence of moisture.

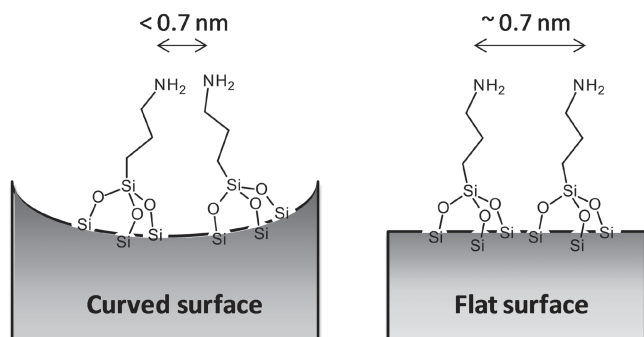
In theory, the CO_2 adsorption capacity of an amine-functionalized mesoporous silica sample should be proportional to the amine content; at a ratio of $\text{N}:\text{CO}_2 = 2:1$, assuming that all CO_2 molecules form carbonates. Therefore, if the amine groups are to be extended to diamine or triamine groups, the adsorption capacity should be doubled or even tripled. Also, a propylamine group on APTES is relatively small ($\approx 0.5 \text{ nm}$ in length) when compared with the diameter of mesopores ($\approx 2\text{--}10 \text{ nm}$). There are unused space inside these “monoamine” functionalized mesoporous silicas. Consequently, scientists had been exploiting this space by using polyamine groups, $-(\text{CH}_2\text{CH}_2\text{NH})_n-$, to create a surface with multilayered amines for further enhancing the CO_2 adsorption capacity.^[88] Unfortunately, the increase in capacity was much lower than expected.^[89] There are several possible reasons. First of all, these groups can be closely packed on a concave surface with approximately 0.7 nm between groups (see Figure 6), while a CO_2 molecule is about 0.23 nm wide. At such a comparable dimension, the CO_2 molecules adsorbed to the amines on the outer layer may block the others from interacting with the inner amine groups. Moreover, when the density of amine groups increases, the competition for protons in a “moist” environment also increases.^[90] This results in a fraction of amine groups being un-protonated (or less basic) and reduces their affinity towards CO_2 .

Nevertheless, scientists still attempted to fill these mesopores with polyamines to maximize the CO_2 adsorption capacity, notably using polyethyleneimine (PEI). For example, PEI has been immobilized onto SBA-15 via the wet impregnation method and the resultant composite material show an enhanced CO_2 adsorption capacity of 4.89 mmol g^{-1} .^[91] However, PEI is a water soluble polymer and these composite materials can be unstable to gas streams with a high moisture content, particularly for prolong use. Therefore, an alternative method for PEI immobilization is necessary to produce a

Table 3. Selected studies on using functionalized mesoporous silica as the adsorbent for CO₂. All CO₂ adsorption measurements were recorded at 1 atm.

Mesoporous silica type	Amine groups ^{a)}	Functionalization method	BET surface area [m ² g ⁻¹]	Pore volume [cm ³ g ⁻¹]	N concentration [mmol g ⁻¹]	CO ₂ adsorption capacity [mmol g ⁻¹]	Temp [°C]	Ref.
MCM-48	mono	post synthesis	–	–	2.3	2.05	25	[72]
MCM-48	penta + diethanolamine	impregnation	572	0.41	–	0.4	25	[73]
MCM-48	PEI (600)	post synthesis ^{b)}	58.4	0.02	5.2	0.4	25	[74]
MCM-41	mono	post synthesis	17	0.04	2.48	1.15	30	[75]
MCM-41	mono	post synthesis	239	0.04	3.0	0.57	25	[76]
MCM-41	mono	post synthesis	727	0.22	2.35	0.83	25	[77]
MCM-41 ^{c)}	tri	post synthesis	429	1.05	7.8	2.28 ^{d)}	25	[78]
MCM-41	PEI (423)	impregnation	11	0.03	15.5 ^{e)}	2.03	75	[79]
MCM-41	PEI ^{f)}	impregnation	4.2	0.011	15.5 ^{e)}	4.89 ^{g)}	75	[80]
SBA-12	mono	post synthesis	416	–	2.13	1.04	25	[76]
SBA-15	mono	post synthesis	134	–	2.72	1.54	25	[76]
SBA-15 ^{f)}	mono	post synthesis	374	0.54	2.61	0.66	60	[81]
SBA-15 ^{f)}	di	post synthesis	250	0.40	4.61	1.36	60	[81]
SBA-15 ^{f)}	tri	post synthesis	183	0.29	5.80	1.80	60	[81]
SBA-15	PEI (423)	impregnation	80	0.20	15.5 ^{e)}	3.18	75	[79]
MSU-1	penta	impregnation	0.72	0	13.23	3.87	75	[82]
KIT-6	PEI (600)	impregnation	86	0.18	17.3	1.79	25	[77]
MCF	mono	post synthesis	289	1.85	2.55	0.78	45	[83]
MCF	mono	post synthesis	407	1.3	3.4	0.8	75	[84]
MCF	di	post synthesis	183	1.21	2.46	1.25	45	[83]
MCF	tri	post synthesis	139	0.7	4.0	1.3	75	[74]
MCF	penta	impregnation	12	0.1	12.9	4.5	75	[74]
MCF	PEI (423)	impregnation	70.8	0.46	15.5 ^{e)}	3.45	75	[85]
MCF	PEI (800)	impregnation	201	1.54	6.25	1.26	45	[83]
MCF	PEI (3335)	aziridine polymerization	350	2.12	3.48	0.51	23	[86]

^{a)} Key for functional groups: mono = Pr–NH₂ (3-aminopropyl); di = Pr–NH–CH₂–CH₂–NH₂ (N-(2-aminoethyl)-3-aminopropyl); tri = Pr–NH–CH₂–CH₂–NH–CH₂–CH₂–NH₂ (3-[2-(2-aminoethylamino) ethylamino]propyltrimethoxysilane or diethylene amine, DETA); penta = NH₂–CH₂–CH₂–NH–CH₂–CH₂–NH₂–CH₂–CH₂–NH–CH₂–CH₂–NH₂ (tetraethylenepentamine); PEI = –(NH–CH₂–CH₂)_n– (polyethyleneimine); ^{b)} PEI grafted onto a propylchloride-functionalized MCM-48; ^{c)} Pore-expanded MCM-41 using post-synthesis hydrothermal treatment with *N,N*-dimethyldecylamine (DMDA) at a temperature of 120 °C for 72 h; ^{d)} Measured at 5% CO₂ in N₂, 1 atm; ^{e)} Estimated from 50 w/w% PEI; ^{f)} *M_w* of PEI not provided; ^{g)} Calculated from 215 mg CO₂ g⁻¹ PEI.

**Figure 6.** Schematic illustration on the distance between propylamine groups on a flat and curved silica surface.

PEI-mesoporous silica composite which is stable under a high moisture environment. Drese et al. reported a procedure to prepare PEI-mesoporous silica composite via polymerization of aziridine inside the mesopores.^[92] Although the composite material showed a good adsorption capacity, aziridine is a highly toxic and penetrative chemical and therefore, the method is rather unsustainable. Kumar et al. grafted PEI onto a MCM-48 support functionalized with propylchloro groups (Pr-Cl) but a low CO₂ adsorption capacity (0.4 mmol g⁻¹) was recorded due to pore blockage.^[93]

As with both MOFs and zeolites, for a supported amine adsorbent to be considered suitable for use in CCS on an industrial scale it has to be able to be fully regenerated and be able to undergo adsorption-desorption on a rapid timescale. In general

these supported amine adsorbents with a full desorption of CO₂ can be regenerated by selecting the right desorption conditions, usually at a lower temperature (70–150 °C) and atmospheric pressure, which circumvent the regeneration problems associated with the CaO- or MgO-modified mesoporous silicas (at >700 °C). Moreover, Chaffee et al. have shown that propylamine-functionalized hexagonal mesoporous silicas (HMS) can be regenerated at a temperature as low as 20 °C (293 K) under a fully anhydrous argon purge.^[94]

Unlike MOFs, research on scaling up the production of mesoporous silica has seen much progress. First, mesoporous silicas can be prepared at room temperature and pressure;^[95] this helps in scaling up the synthesis. Moreover, continuous synthesis of mesoporous silica with a highly ordered 2D hexagonal (*P6mm*) structure has also been reported.^[96] Large scale production of mesoporous silica for industrial use is therefore possible. In terms of environmental impact, functionalized mesoporous silicas do not rely on toxic metals or ligands for the adsorption of CO₂. However, one concern will be on the tethered amine groups; the environmental impact of these groups is still unknown. Moreover, and more importantly, the template used for preparing mesoporous silica cannot be ignored. It can only be removed either by calcination or solvent extraction. A considerable amount of CO₂ is to be emitted upon calcination while extraction of template generates unwanted solvent waste. Therefore, in order to lower the carbon footprint for using mesoporous silica, template-free synthesis should be considered.^[97]

4.4. Carbon Nanotubes and Ordered Mesoporous Carbon

Nanoporous carbon materials, including activated carbons and carbon fibers, have also been considered as adsorbents for CO₂, because of their hydrophobic nature and high surface area;^[98] both properties make them suitable for CCS purpose. Moreover, many carbon materials are light in weight and relatively cheap to manufacture (except carbon nanotubes).^[99] Therefore, they have many industrial uses including water purification and decolorization.^[100] Among all carbon materials, carbon nanotubes (CNT, single-walled or multiwalled) have been extensively studied as an adsorbent for carbon dioxide. For example, multiwalled carbon nanotubes have shown a CO₂ adsorption capacity of $\approx 0.5 \text{ mmol g}^{-1}$ ($22.7 \text{ mg CO}_2 \text{ g}^{-1}$) with an increase to $\approx 0.9 \text{ mmol g}^{-1}$ after grafting with amine groups using APTES.^[101] However, silanization using APTES could be wasteful for this expensive carbon material because such a CO₂ adsorption capacity can be easily achieved by other APTES functionalized materials, e.g., mesoporous silica (see Section 4.3) or even commercial fumed silica. Furthermore, many of the CO₂ adsorption studies using carbon nanotubes are based on computer simulations rather than real adsorption experiments.^[102] One reason is that, unlike other bulk nanoporous carbon materials, carbon nanotubes are expensive to prepare although continuous production has been reported.^[103] This is also likely to be the main obstacle for carbon nanotubes to be used as a CO₂ adsorbent on an industrial scale.

Another family of nanoporous carbon materials is the ordered mesoporous carbon, prepared from mesoporous silica

templates. By carbonizing ordered mesoporous silicas and then removing the silica templates using a strong base (KOH or NaOH) or HF, a mesoporous carbon material with an “inverse” structure of the template itself can be formed.^[104] In terms of adsorption chemistry, these materials have similar characters to carbon nanotubes. Therefore, they have been used for CO₂ adsorption and separation. For example, the CO₂ adsorption capacity of mesoporous carbon CMK-3 (template with SBA-15) and CMK-8 (template with KIT-6) were recorded at 2.4 and 2.1 mmol g⁻¹ (25 °C and 1 atm) respectively.^[105] An enhanced CO₂ adsorption capacity was demonstrated by a treatment using KOH followed by heating. However, details for the chemical effects on the material surface due to this treatment were not discussed in this report. Similar to mesoporous silicas, in order to enhance the CO₂ adsorption capacity, polymers with basic characters have been immobilized inside the pores of mesoporous carbon.^[106] It was found that PEI-loaded CMK-3 composites showed a maximum adsorption capacity of 3.13 mmol g⁻¹, compared with 1.55 mmol g⁻¹ recorded from a pure carbon CMK-3 sample. As shown from both mesoporous silica and mesoporous carbon, polyamine-loaded composite materials are promising candidates for CCS purpose.

Although scaling up production of these ordered carbon nanomaterials at a possible kilogram-scale production has been reported,^[107] the more suitable candidate among this group of carbon materials for CO₂ adsorption is still microporous activated carbon. This is mainly because their production cost and scale of preparation are much more realistic for large scale applications. Activated carbons can be prepared from various plant wastes, such as nutshells and wood, or other bulk sources (e.g., peat and coal) by heating (or carbonizing) the precursors at a high temperature (up to 900 °C) in the absence of oxygen. Usually, a surface area of 200–500 m² g⁻¹ can be achieved for most activated carbon. However, since these carbon-based materials are neutral or mildly acidic on surface, they need further chemical modification to be made selective for CO₂ adsorption. Amination of activated carbon is one popular method for modifying the surface in order to enhance the selectivity towards CO₂ due to the improved surface basicity.^[108] Unfortunately, the extend of amination depends on the reaction temperature and extensive heat (up to 800 °C) is usually required. These two energy-intensive steps (carbonization and amination) for preparing basic activated carbon are likely to hamper their sustainable, long-term use for CO₂ capture.

4.5. Other Nanoporous Materials for CO₂ Capture

In the past few years, new types of porous organic nanomaterials have caught the attention of many research groups. Organic cage framework (OCF) materials consist of repeated units of cage-like ordered structures, similar to MOF systems.^[109] Unlike MOFs, these OCFs are purely organic without any metal component. The specific cage size seems to have a significant effect on the separation of CO₂ from other gases, such as nitrogen. For instance, the OCF material formed from 1,3,5-tris(4-aminophenyl)benzene and isophthalaldehyde showed a high CO₂ adsorption capacity of 2.71 mmol g⁻¹ ($60.7 \text{ cm}^3 \text{ g}^{-1}$) at 0 °C, as well as a high CO₂ selectivity over N₂.^[110] Moreover,

many of these OCF materials are prepared by coupling amine compounds, which can provide a large number of binding sites for CO₂.

Covalent organic frameworks (COFs), another class of porous organic nanomaterials, are frameworks formed from molecules which are able to react with one another via strong covalent bonds. As with MOF synthesis the building blocks used for COFs are designed to interact with one another in a way to promote a propagation of the framework, and is achieved through using rigid building blocks with divergent functionalities, for example tetra(4-dihydroxyborylphenyl)methane (TBPM), and its silane analogue (TBPS), both rigid tetrahedral molecules containing 4 boronic acid groups. These molecules are able to either to undergo a self-condensation reaction to form a structured framework, or a co-condensation reaction with a different building unit such as hexahydroxytriphenylene (HHTP), which has a rigid triangular shape, thus leading to a different COF system.^[111] It has been shown that COFs can contain similar sized pores (0.9 nm–3.2 nm) to many MOFs and indeed both COF-105 and COF-108 were shown to have a very low density (as low as 0.17 g cm⁻³), which is lower than many highly porous MOFs. While there are still relatively few experimental gas adsorption studies on COFs it has been shown by simulation studies that large CO₂ adsorption capacities may be achievable with certain COFs.^[112]

Recently another type of purely organic framework, known as a supramolecular organic framework (SOF), has been reported to show interesting reversible gas adsorption properties.^[113] A SOF system is a crystalline porous material stabilized through exploiting non-covalent interactions such as hydrogen bonds and π - π stacking interactions. However, because these interactions are inherently weaker than coordinate or covalent bonds, few target molecules have been discovered that can successfully form a framework that is stable to solvation. Nonetheless, as with OCFs and COFs, the ability to eliminate the need of a source of metal in the synthesis of SOFs offers the possibility to develop some extremely low-density solid adsorbents.

Despite their considerable potential, research in OCF, COF and SOF systems is still relatively in its infancy compared to the much more widely studied systems of zeolites, MOFs and supported amines. Therefore additional effort is still required to make any of these porous organic frameworks a realistic candidate for CO₂ capture on an industrial scale. As with other adsorbent materials discussed earlier, production of these materials has to be scalable while the environmental impact of these organic materials has to be scrutinized carefully.

5. Catalytic Conversions of CO₂ as New Pathways for Carbon Capture and Utilization (CCU)

As research on adsorbents for CCS has been expanded rapidly in recent years, many nanoporous materials with excellent adsorption capacity, selectivity and stability have been reported. However, CCS technologies based on adsorbents are still limited by their adsorption capacity. Instead of just simple “capture and storage”, CO₂ can be transformed into important chemical products via various CO₂ activation reactions. As such, the “capture process” is not limited by the adsorption capacity of the

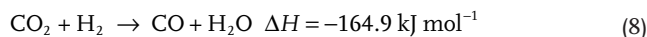
adsorbents, which is now approaching saturation. Since CO₂ is a very stable compound thermodynamically, catalysts are usually required to activate CO₂ molecules to form other compounds, mainly organics. In nature, one notable catalytic process has been regulating the CO₂ content in our atmosphere; photosynthesis is a very efficient catalytic process to convert CO₂ into carbohydrate. Unfortunately, under the current CO₂ emission rate, photosynthesis from plants simply cannot cope, and it is further hampered by continuous global deforestation. Therefore, scientists have also been actively investigating other catalytic processes for CO₂ transformations, or commonly termed as “carbon capture and utilization” (CCU).

5.1. Catalytic Activation of CO₂

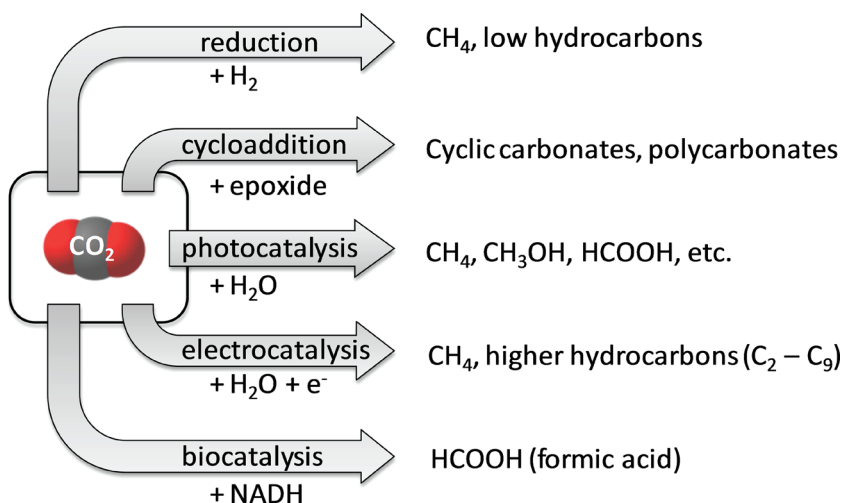
Despite its chemical stability, there are several pathways for catalytic CO₂ activation showing some potential in tackling the CO₂ problem. For example, CO₂ has been reacted with various unsaturated hydrocarbons (alkenes and alkynes) to form carboxylic acids and esters in presence of homogeneous catalysts such as Ni(acac)₂ (nickel(II) acetylacetonate) and Ni(cod)₂ (bis(cyclooctadiene)nickel) via a reductive carboxylation reaction.^[114] This includes the synthesis of an important chemical, acrylic acid, from CO₂ and ethylene. Another homogeneous catalyst (Zn complexes) has been used to catalyze the synthesis of polycarbonates from CO₂ and epoxides.^[115]

However, these examples involve use of homogeneous catalysts, which are usually associated with high energy consumption, high waste emission and poor recyclability. Use of heterogeneous catalysts for CO₂ conversion can circumvent many problems associated with homogeneous catalysis but usually shows a lower reaction rate and poorer selectivity. For instance, a mesoporous adenine-modified Ti-SBA-15 catalyst was shown to be active for the conversion of CO₂ to cyclic carbonates in presence of an epoxide but high pressure (6.9 atm) was required.^[116]

In industry, large scale catalytic processes involving the use of CO₂ as a feedstock are also available. One classic example is the conversion of CO₂ with H₂ to form CO and H₂O in a low-temperature water-gas shift reaction, which is widely used in the fuel industry.^[117] A supported copper on zinc oxide catalyst, with a Cu:Zn molar ratio = 1:2, is considered as the most suitable for this reaction.



Alternatively, the use of photocatalysts can convert CO₂ to various simple compounds including methanol, CO and methane.^[118] Although photocatalysis resembles the preferred photosynthesis process, these products are far from ideal for consideration by industries, where much more efficient processes are available for the production of methanol and CO. On the other hand, methane is usually not industrially manufactured because of the abundant natural gas available globally. Also, methane is considered as another greenhouse gas with a greenhouse effect 25 times higher than CO₂. Therefore, transforming CO₂ to methane does not really solve our greenhouse gas problem.



*cycloaddition of CO₂ onto epoxide to form cyclic carbonate:

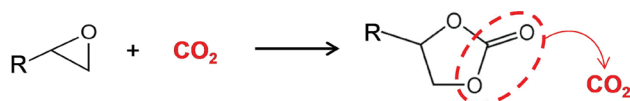


Figure 7. Summary on available pathways for catalytic conversions of CO₂ to various chemicals suitable for CCU purpose.

While many of the large-scale CO₂ conversion processes have already been well optimized in terms of choice of catalysts, reaction temperature and pressure, operational cost, and reactor/process design, new catalysts are being developed for small laboratory-scale conversions but the products need to be of a high value or high importance for justification. Therefore, it could be challenging to develop new nanoporous catalysts to outperform these commercial catalysts when all these operational parameters need to be considered. Nonetheless, **Figure 7** highlights five classes of CO₂ conversion reactions that could involve the use of nanoporous catalysts.

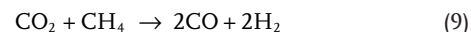
5.2. Nanoporous Catalysts for CO₂ Conversion

Many nanoporous materials have been widely used as heterogeneous catalysts. Notably, zeolites such as ZSM-5 and zeolite-Y (faujasite, FAU) are commonly used as solid acid catalysts for hydrocarbon cracking and isomerization.^[119] On the other hand, research on the catalytic applications of MOFs^[120] and functionalized mesoporous silicas^[60] can also be found in the literature. As discussed in Section 4, nanoporous materials usually have a high BET surface area, which is a positive feature for heterogeneous catalysis. Such advantage is of course beneficial to CO₂ conversion reactions.

5.2.1. Zeolites for CO₂ Conversion

Because of their established applications in petroleum industries, the catalytic properties of zeolites have been tested on a

number of hydrocarbon formation reactions using CO₂, notably reformation of methane. In this methane reforming reaction, hydrogen (H₂) is produced in addition to CO (see Equation 9); these are the components for syngas.



A supported Ni catalyst is commonly used for this reaction, sometimes with a promoter, such as Al₂O₃, CaO, MgO or CeO_x. For example, Ni supported on zeolite, with CaO and K₂O promoters, has shown a high activity as well as a high resistance to coke formation.^[121] Selected examples of methane reformation studies using zeolite catalysts are summarized in **Table 4**. This process represents a possible “reverse” mechanism for the combustion of fossil fuels by converting CO₂ back to fuels (H₂ and CO). However, the high energy consumption for methane reforming must be considered due to the high temperature (600–800 °C) for process operation. Other examples of using zeolites in CO₂ conversion to bulk chemicals include CO₂ hydrogenation to form methanol in a zeolite (zeolite A) membrane reactor^[133] and, by further reacting with in situ formed methanol, to produce dimethyl ether over a Cu–ZnO–ZrO₂/H-ZSM5 catalyst.^[134]

In addition to industrial processes for bulk chemicals, modified zeolites, acting as base catalysts, have also shown ability to promote cycloaddition of CO₂ to epoxides. Potassium exchanged zeolite X (or KX) loaded with Cs⁺ ions have shown a high activity for adding CO₂ onto ethylene oxide to form ethylene carbonate (reaction equation shown in Figure 5).^[135] which is a useful chemical as a plasticizer as well as an electrolyte in lithium batteries. However, because of the small pore size of zeolite X (≤1.2 nm), the activity for converting larger reactants such as epoxypropylbenzene was much lower. This is a common limitation for using zeolites as catalysts as only small molecules of both reactants and products are applicable.

5.2.2. MOFs as Catalysts

Catalysis using MOFs is not as common as zeolites due to the lower thermal stability of the MOFs. Unlike zeolites, the metal centers of MOFs, particularly those constructed with transition metals, can act as catalytic active sites for organic transformation reactions. Regarding using CO₂ as a feedstock, several MOF systems have been found active for cycloaddition reactions with epoxides. For example, MOF-5 was shown to be active in the cycloaddition of CO₂ onto propylene oxide and styrene oxide at 4 atm and 50 °C, in presence of a quaternary ammonium salt, e.g., n-Bu₄NBr.^[136] Indeed, the proposed mechanism suggested that the metal center (Zn₄O) of MOF-5 acted as a Lewis acid for interacting with the epoxide oxygen while the Bu₄N⁺ ion opened the epoxide ring. Therefore, the

Table 4. Selected examples of methane reforming with CO₂ using supported metal on zeolite and mesoporous oxide catalysts for producing syngas.

Nanoporous support	Catalyst components	Mass of catalyst [mg]	GHSV ^{a)} [cm ³ h ⁻¹ g _{cat} ⁻¹]	Temp [°C]	P [atm]	CO ₂ :CH ₄	CO ₂ conversion	Ref.
Zeolites								
Silicate-1	Ni	200	30 000	700	1	1:1	80–84%	[122]
BEA	Ni/Rh	200	30 000	700	1	1:1	77–78%	[123]
BEA	Ni/Pt	70	85 700	640	1	1:1	26–31% ^{b)}	[124]
Y	Ni/Pt	70	85 700	640	1	1:1	26% ^{b)}	[124]
Y	Ni	200	30 000	700	1	1:1	90%	[125]
ZSM-5	La ₂ NiO ₄	100	48 000	800	1	1:1	77%	[126]
Mesoporous oxides								
SBA-15	Ni/MgO-Al ₂ O ₃	300	12 000	800	1	1:1	85%	[127]
SBA-15	Ni/MgO	100	36 000	550–800	1	1:1	25–83%	[128]
SBA-15	LaNiO ₃	100	36 000	550–800	1	1:1	30–80%	[129]
MCM-41	LaNiO ₃	100	36 000	550–800	1	1:1	30–80%	[129]
SBA-16	Ni/CeO ₂	20	25 500	700	1	1:1	68–72%	[130]
Mesoporous Al ₂ O ₃	Ni/CeO ₂	100	36 000	550–800	1	1:1	38–85%	[131]
Mesoporous Al ₂ O ₃	Ni/MgO	100	15 000 – 60 600	600–800	1	1:1	95%	[132]

^{a)}GHSV = gas hourly space velocity; ^{b)}CO₂ conversion data was not supplied, figures shown were CH₄ conversions.

quaternary ammonium can be viewed as a co-catalyst and the activity seemed to have a direct relationship to its solubility in the epoxide reactant. Although the MOF-5 solid can be reused, the Bu₄N⁺ ions are unlikely to be recovered easily, raising a real question over sustainability. Co-MOF-74 has also been tested in a similar reaction, addition of CO₂ onto styrene oxide, but without a co-catalyst.^[137] A 96% conversion was observed in 4 h but the reaction was operated at elevated pressure and temperature (20 atm and 100 °C). Also a toxic solvent, chlorobenzene, is required. This research group has also compared the activity of selected MOF systems for the cycloaddition of CO₂ onto styrene oxide and among them, UIO-66-NH₂ MOF was found to be the most active, with 70% conversion in 1 h.^[138] However, the reaction conditions remained at high pressure and temperature with the use of a toxic solvent.

There are other examples showing the catalytic activity of MOFs (Ni(salphen)-MOF,^[139] Mg-MOF-74,^[140] ZIF-8^[141] and MIXMOF-5^[142] as catalysts for cycloaddition of CO₂ onto an epoxide. Compared with zeolite catalysts, the larger pores of MOF catalysts did promote cycloaddition of CO₂ on larger epoxides, but most of these systems were operated at high pressure (>5 atm) and temperature (100–140 °C), with quaternary ammonium ions as co-catalysts in some cases. Despite the superiority in selective CO₂ adsorption, MOFs' potential as catalysts for CCU still seems rather limited.

5.2.3. Functionalized Mesoporous Silica Catalysts

Catalytic applications using functionalized mesoporous silicas is widely available in the literature,^[60] partly due to their large pore dimensions available for accommodating larger organic reactants and products, as well as facilitating their diffusion into and out of the catalyst. For CO₂ conversions, this property

is advantageous because the target products are mostly larger organic molecules (>1 nm), which may block smaller pores of zeolites and MOFs.

For example, dry reformation of methane with CO₂ using nickel nanoparticles supported on mesoporous silica catalysts have been reported as early as 2006.^[143] Table 4 summarizes several selected examples published since 2013. Although many of these catalysts showed good resistance to deactivation over a long period of continuous use (e.g., 80 h), there was a lack of direct comparison on the catalytic performance among these mesoporous catalysts. It is difficult to pinpoint which is the best composition for methane reformation or which parameters are critical for an efficient process. In industry, dry reformation of methane is still not commonly used due to the coke formation and subsequent catalyst deactivation,^[144] which was shown to be minimized using these mesoporous silica-based catalysts. Therefore, more research in this area may lead to some breakthrough for methane reformation using CO₂ in industry.

Mesoporous silicas have also been used as a support for photocatalysts (e.g., TiO₂) for the conversion of CO₂ to methane and methanol. For example, Ti-doped MCM-41 and MCM-48 were found to be active in the conversion of CO₂ in water to form both methane and methanol, at a 3:1 ratio;^[145] this is in contrast to the low activity and low selectivity towards methanol shown from bulk TiO₂. A photocatalyst prepared by impregnating TiO₂ nanoparticles into the cages of FSU-16 mesoporous silica was also active in converting CO₂ to a mixture of methane and methanol.^[146] However, it is well-known that TiO₂ species only adsorb UV radiation while doping with other transition metals, such as Cu, is required for the adsorption of visible energy.

In addition to conversion to simple molecules such as methane and methanol, cycloaddition can also be catalyzed using catalysts supported on mesoporous silica. The reactions are essentially the same as those presented previously for

catalysis using MOFs. Similar to some MOF systems for this reaction, a positively charged species (e.g., Bu_4N^+) is required to activate the epoxide ring. In these mesoporous silica systems, positively charged groups can be grafted onto the silica surface via silanization. For example, imidazolium ions have been supported onto the MCM-41 surface via a three-step grafting method.^[147] This catalyst was shown to be active for the formation of cyclic carbonate from epoxides (styrene oxide and allyl glycidyl ether) and recycling of catalyst showed insignificant deactivation. However, also similar to the MOF systems, a high pressure of CO_2 (7–40 atm) was required for the reactions. Therefore, the sustainability of these processes is once again questionable.

5.2.4. Modified Carbon Nanotubes for CO_2 Conversion

Although carbon materials have been widely used as supports for metal catalysts (e.g., Pd/C and Pt/C), use of carbon nanotubes (CNTs) for catalysis is rare because of the high cost associated with production. In many cases, other carbon materials, such as activated carbon and carbon nanofibres, are preferred materials for supporting metal catalysts.^[148] Nonetheless, use of CNTs as a support for catalysts is still possible, including use in catalytic conversion of CO_2 . For example, transition metal (Ni and Fe) supported on multiwalled CNTs (MWCNTs) have been used to convert CO_2 into hydrocarbons, including methanation reaction.^[149] Ni/MWCNTs (10% Ni) have shown a conversion (<50%) of CO_2 with nearly 100% selectivity towards methane at 500 °C in presence of H_2 . Addition of La (1%) has shown an increase in conversion up to 60%. However, the study did not include comparison on activity with other activated carbon-based catalysts. Therefore, it would be difficult to assess the advantage of using CNT as a catalyst support material. O'Byrne et al. showed that a Fe/MWCNT catalyst prepared by growing the CNT support on Fe nanoparticles was active for CO_2 conversion, in presence of H_2 , with selectivity towards higher-order hydrocarbons, with 24.3% C_2 – C_4 hydrocarbon formed.^[150] The formation of higher hydrocarbons is certainly encouraging but this study also lacks comparison with other conventional carbon-based catalysts.

MWCNT supported TiO_2 catalysts have also been used as photocatalysts for the reduction of CO_2 with water.^[151] In this study, the catalyst preparation was found to have a significant influence on the product selectivity; TiO_2 /CNT prepared from a sol-gel/precipitation method is selective towards the formation of ethanol while formic acid is the main product from the catalyst prepared via a hydrothermal method. This is because the TiO_2 formed from sol-gel/precipitation was mainly anatase while an increased amount of rutile phase was found in the sample prepared from the hydrothermal method. When compared with use of activated carbon support, only a marginal improvement was observed from using CNT as catalyst support. Such result raises a question mark over using this CNT-supported catalyst for a large scale CO_2 conversion.

Compared with other nanoporous materials, CNTs are superior in terms of electroconductivity. Therefore, it can be used as materials for electrodes in electrocatalytic conversion of CO_2 . Genovese et al. have found the formation of higher

hydrocarbon (up to C_8 – C_9) using electrodes based on Fe nanoparticles supported on CNT.^[152] Further enhancement was achieved by doping the CNT with nitrogen. There is no evaluation on the electricity consumption presented in this report so it is difficult to assess the viability of this method as a carbon dioxide re-utilization.

6. Conclusion and Future Outlook

The current CCS landscape is still heavily directed to capture followed by geological storage. For example, “concentrated” CO_2 from post-combustion capture is transported to designated reservoirs and stored underground. However, these CO_2 reservoirs are not simple ecological panaceas as industrial accidents and natural leaks could cause disasters similar to that at Lake Nyos, Cameroon in 1986^[153] can happen. Moreover, these capture-storage coupling projects are costly, estimated to around 150–200 GBP (\approx 250–330 USD) per MWh,^[154] although this figure is likely to be reduced when full-scale CCS facilities are to be built in the next few decades. Considering such a high operational cost for these CCS technologies, using nanoporous materials as CO_2 adsorbents could only further increase this financial burden and therefore they are unlikely to be practical until a significant reduction in cost for preparing these adsorbents is shown. These are considered as non-recoverable costs and likely to be loaded onto the already high production cost for energy in many countries. Sustainability of the whole capture and storage process is therefore somehow dubious.

On the other hand, if CCU technologies are mature for large-scale operations, the potential hazard of CO_2 reservoirs can be avoided. Furthermore, the products formed from catalytic conversions of CO_2 can be sold and therefore can compensate part of the operational cost for CO_2 capture. Since many of these reactions are operated with a pure CO_2 feed or at a high CO_2 content, sorbent materials may still be required to capture CO_2 from flue gas for pre-concentration. Therefore, the catalytic reactor may have to be constructed near a power station fitted with CO_2 capture facilities. This may cause some engineering challenges. In economical terms, although some cost can be recovered, bulk products such as methanol and hydrocarbons are unlikely to provide financial security for the operation. Consequently, CCU processes towards fine chemical products, such as organic carbonates, will be much more likely to succeed.

Despite the large amount of research, CCS and CCU technologies are still regarded as short-term to mid-term solutions for tackling ever increasing CO_2 emission into the environment. Ultimately, our society has to move away from the reliance on fossil fuels for energy generation. Renewable energy sources, such as solar energy, wind energy, hydropower, and wave energy, are all considered to have potential. However, we should still be cautious before rapidly implementing any new technology as all implications, particular in the long-term, should be considered to prevent any unexpected damaging and potentially irreversible effects, such as the over-plantation of oil palms for bio-diesel and the subsequent massive deforestation.^[155] Nonetheless, current and future CCS systems could act as an important stop gap while scientists continue the intense research required to fully develop new sustainable technologies

for low carbon power generation to tackle the global problem of anthropogenic climate change.

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